

DEPOSITION OF AlN THIN FILMS BY MAGNETRON REACTIVE SPUTTERING

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AlN films were deposited onto silicon substrates in d.c. planar magnetron system by means of reactive sputtering of aluminium in an atmosphere of nitrogen.

The influence of the deposition conditions and of post-deposition annealing on the properties of the insulator and the AlN-Si interface were investigated.

1. INTRODUCTION

In recent years considerable interest has been shown in the use of thin films of nitrides as high temperature dielectrics with properties suitable for semiconductor technology. AlN is one of the most interesting nitride films because of its wide band gap (6.3 eV), high decomposition temperature (2490 °C) and chemical stability (it is stable in air up to 700 °C). As a piezoelectric material with good dielectric properties, such as low losses, good high frequency characteristics, high sound velocity (6×10^3 m s⁻¹) and coupling coefficient ($k^2 = 0.8\%$), AlN is a promising material not only for the passivation of semiconductor surfaces and as an insulator for high temperatures but also for thin film transducers and surface acoustic wave devices¹⁻⁴.

Near contact between a piezoelectric material and a semiconductor is used in some surface acoustic wave devices such as convolvers, correlators and scanistors. Because of the good piezoelectric properties of AlN the AlN/Si system is very promising in this respect, and it is important to study its properties in MIS structures.

Thin films of AlN have been prepared by several techniques: chemical vapour deposition⁵⁻⁸, reactive sputtering⁹⁻¹², reactive evaporation^{13,14}, nitriding of evaporated aluminium in a glow discharge in nitrogen^{15,16} and ion implantation¹⁷.

Owing to its high productivity and the high quality of the films produced, magnetron cathode sputtering has found wide application lately. However, the use of magnetron sputtering in a reactive gas has only recently been investigated. Only one article¹⁸ has reported the preparation of thin films of AlN with good acousto-electric characteristics by means of r.f. magnetron reactive sputtering.

In the present study, thin films of AlN were deposited by means of reactive sputtering in a d.c. planar magnetron system onto heated and unheated silicon substrates. The influences of the deposition conditions and of post-deposition

annealing in nitrogen and hydrogen on the properties of Si/AlN MIS structures were studied.

2. PREPARATION OF AlN FILMS

Films of AlN were prepared in a d.c. planar magnetron system by means of reactive sputtering. The cathode-to-anode distance was 50 mm. The aluminium target had a purity of 99.99% and a diameter of 70 mm. Substrates of n-type silicon with a resistivity of $5 \Omega \text{ cm}$ were cleaned by a standard procedure of MIS technology and were placed on the anode plate.

The ultimate pressure of the vacuum system was $(1-50) \times 10^{-6}$ Torr. After appropriate cleaning the nitrogen sputtering gas was introduced into the reaction chamber. The deposition parameters were as follows: nitrogen pressure, 10^{-2} Torr; discharge voltage, 300–350 V; substrate temperatures, about 60 and 300 °C.

In order to obtain films of high quality, a suitable power (2 W cm^{-2}) was chosen such that the deposition rate was about 100 Å min^{-1} ¹². Films of thickness 1000–2000 Å, as measured by laser ellipsometry (at a wavelength λ of 632.8 nm), were deposited.

3. RESULTS

3.1. Dissolution rate

Concentrated hydrofluoric acid did not attack AlN. The deposited AlN films were soluble in phosphoric acid. At temperatures of up to 40 °C the dissolution rate of AlN was negligible. At 70 °C the dissolution rate of AlN in H_3PO_4 was 28–40 Å s^{-1} and was independent of substrate temperatures up to 300 °C. After heat treatment of the films in nitrogen for 30 min at 1000 °C the dissolution rate decreased to less than 1 Å s^{-1} , indicating that at this temperature considerable densification of the films had taken place.

3.2. Optical properties

The refractive index n , as measured by laser ellipsometry ($\lambda = 632.8 \text{ nm}$), was found to be 1.70–1.90 and did not change visibly after annealing in hydrogen at 400 °C and in nitrogen at 1000 °C.

The IR transmission spectra of the AlN films showed an absorption band at 675 cm^{-1} . This frequency agreed with other measurements¹¹.

3.3. Dielectric properties of Si/AlN/Al structures

Si/AlN/Al MIS capacitors were fabricated to determine the dielectric constant, resistivity and breakdown voltage of the AlN films. The silicon used as the substrate was n type and had a resistivity of $5 \Omega \text{ cm}$. Aluminium electrodes of diameter 0.5 mm were evaporated onto the AlN films. The interfacial properties of the Si/AlN system were examined on the same capacitors.

The dielectric constant ϵ was evaluated from the high frequency (1 MHz) capacitance of MIS structures in strong accumulation and the thickness of the AlN films measured by ellipsometry. ϵ was found to be in the range 7–10. A definite

dependence of ϵ on the substrate temperature and on post-deposition annealing could not be established.

The resistivity of the films measured at 10^5 V cm^{-1} varied from 2×10^{14} to $6 \times 10^{14} \Omega \text{ cm}$.

The breakdown field of the AlN films was about $5 \times 10^6 \text{ V cm}^{-1}$ and did not depend on the substrate temperature up to 300°C or on post-deposition annealing.

3.4. *C-V measurements*

High frequency (1 MHz) *C-V* characteristics were measured to gain information about electrically active defects in the insulator and at the interface of the Si/AlN structures.

Unlike the SiO_2 layers, which are always amorphous, the deposited AlN layers are usually polycrystalline or convert into that form during the subsequent treatments^{11,18}. It was interesting to establish how this behaviour as well as the piezoelectric properties of AlN affected the properties of the structure, as determined from the *C-V* characteristics, and also what role hydrogen played in the case of AlN. In published articles about AlN films *C-V* measurements have rarely been considered^{11,17}.

In the present study *C-V* characteristics were measured at a frequency of 1 MHz before and after various heat treatments.

Figure 1, curve a, shows a *C-V* curve for an Si/AlN/Al structure in which the AlN layer was prepared without additional heating of the substrate. The curve was obtained immediately after metallization without annealing. It is similar to the curves for standard Si/ SiO_2 structures before annealing but its hysteresis is greater and the direction of the hysteresis loop is opposite, i.e. the negative charge of the insulator increases at negative voltages and the positive charge increases at positive voltages. This type of hysteresis may be due to the presence of mobile charges in the AlN, or to the injection into the AlN of either electrons from the metal electrode or holes from the silicon. In the case of Si/ SiO_2 , for which the direction of the hysteresis loop is opposite to that for AlN, a tunnel exchange of electrons most probably takes place between the silicon substrate and traps in the adjacent region of oxide¹⁹.

The results of Fig. 1, curve a, are not stable. When the measurements are repeated the hysteresis loop moves to the right but its area remains almost the same. After some minutes the curve is stabilized. Sometimes the curves became very steep but this did not indicate a low concentration of interface states because the type of hysteresis which was observed increased the steepness of the *C-V* characteristics.

Figure 1, curve b, shows a typical *C-V* curve from a structure which was annealed for 1 h in a hydrogen atmosphere at 400°C after metallization. This curve is considerably more stable. The hysteresis decreased markedly and it was in the opposite direction, i.e. curve b resembles the curve for an incompletely annealed Si/ SiO_2 structure. In some cases the hysteresis disappeared.

The flat-band voltage was almost always positive and was in the range 4–8 V, indicating the presence of a negative effective immobile charge in the insulator, in contrast with the Si/ SiO_2 structure.

The hysteresis which was observed cannot be due to the movement of impurity ions, e.g. Na^+ , because it is strongly influenced by annealing. The hysteresis probably has an electronic mechanism and is due to the injection, trapping and

re-emission of electrons.

Some samples were annealed in nitrogen at 1000°C for 30 min before metallization. The C - V characteristics obtained after metallization were similar to curve a in Fig. 1 but with a smaller hysteresis. After post-metallization low temperature annealing, the C - V curves became similar to curve b in Fig. 1. Many of the samples were susceptible to breakdown. This was probably due not so much to the growth of the crystallites as to the appearance of microcracks in the films. Our experiments show that high temperature annealing of the films just after deposition did not give positive results.

The same experiments were carried out with samples in which AlN layers had been deposited onto silicon substrates heated to 300°C. The C - V characteristics of such metallized structures without annealing are shown in Fig. 2, curve a. They are similar to those of structures prepared with a low substrate temperature and annealed in hydrogen at 400°C (Fig. 1, curve b). The hysteresis is of the same value (0.5–1 V) and in the same direction. The curves were shifted towards positive voltages and the flat-band voltage was in the range 4–8 V. After annealing in hydrogen at 400°C the hysteresis did not disappear but only decreased to 0.2–0.5 V (Fig. 2, curve b). The flat-band voltage decreased slightly. However, one peculiarity can be observed in the C - V curves: an increase in the capacitance at the beginning of the inversion. This phenomenon can be explained as due to the increase in the effective area of the gate electrode, which occurs because the inversion layer under the electrode comes into contact with the inversion layer outside the electrode which results from the negative charge in the insulator.

Such an increase in capacitance was not observed in the samples which were not annealed (Fig. 2, curve a) nor in those which were annealed but had been prepared at low temperatures (Fig. 1, curve b), where the flat-band voltage was also positive. Probably the increase in the capacitance was masked by the greater concentration of surface states in these samples.

4. CONCLUSIONS

AlN films were deposited by reactive sputtering of AlN in a nitrogen atmosphere in a d.c. planar magnetron system onto silicon substrates which were either unheated or heated to 300°C.

At a nitrogen pressure of 10^{-2} Torr and a deposition rate of 100 Å min^{-1} the deposited films were of good quality. The following results were obtained: dissolution rate, $28\text{--}40 \text{ Å s}^{-1}$; refractive index, 1.70–1.96; dielectric constant, 7–10; breakdown field, $5 \times 10^6 \text{ V cm}^{-1}$; resistivity, $(2\text{--}6) \times 10^{14} \text{ Ω cm}$.

After high temperature treatment of the AlN films in nitrogen the dissolution rate decreased sharply to less than 1 Å s^{-1} because of the densification that had set in.

The C - V characteristics of the Al/AlN/Si system were examined in detail. Immediately after the deposition the structures showed unstable C - V characteristics with considerable hysteresis in a direction opposite to that for the Si/SiO₂ structure. This indicates that an injection of negative charges occurs when negative voltage is applied to the gate, and an injection of positive charges when a positive voltage is applied.

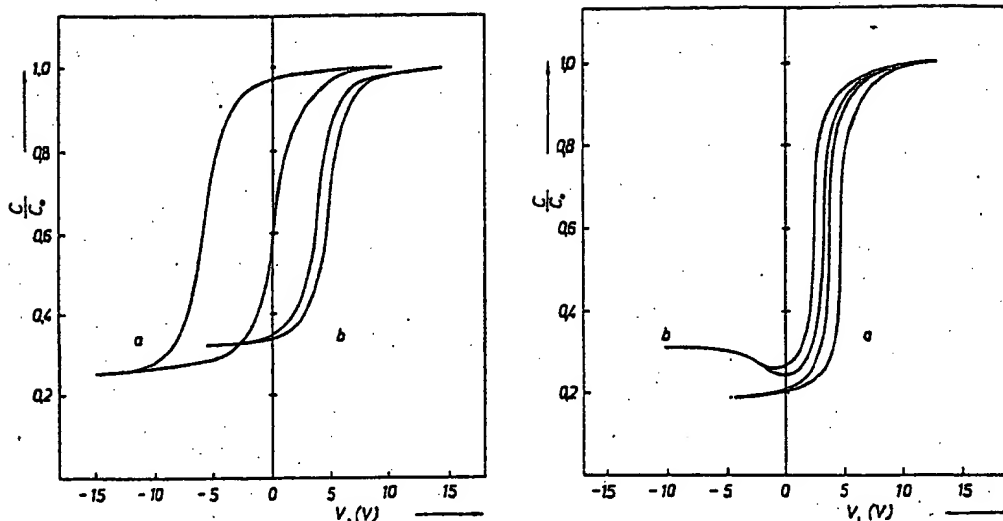


Fig. 1. C-V curves before (a) and after (b) annealing; substrate temperature, about 60 °C.

Fig. 2. C-V curves before (a) and after (b) annealing; substrate temperature, 300 °C.

The C-V curves were considerably stabilized after low temperature annealing in hydrogen; the hysteresis loop became smaller (up to 1 V) and changed its direction. The flat-band voltage is positive, i.e. the incorporated charge is negative, in contrast with the Si/SiO₂ system.

High temperature annealing at 1000 °C in nitrogen had no positive influence on the structures.

The C-V characteristics of structures prepared with substrates heated to 300 °C were similar to those of unheated but hydrogen-annealed devices. Annealing of the heated samples in hydrogen led to an additional improvement in the interface properties of the structures, which was mainly manifested as a decrease in the concentration of surface states.

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